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REMARKS

Applicants respectfully thank the Examiner for indicating that claims 1-7 of this application are allowed. By this response, Applicants have addressed the Examiner's objections made in the *Ex Parte Quayle* Office Action mailed November 3, 2003.

Objections to the Drawings

The Examiner has objected to the drawings as being informal. Applicants are submitting formal drawings with this response. Accordingly, Applicants respectfully request that the Examiner withdraw the objection.

Amendment to the Specification

The Examiner indicates that the application does not comply with one or more requirements of 119(e) and 120 for receiving the benefit of an earlier filing date. Accordingly, Applicants have amended the specification to refer to the prior applications from which the present application claims priority.

Information Disclosure Statement

Applicants thank the Examiner for considering the references in the Information Disclosure Statements (IDS) submitted on July 15, 2002 and November 3, 2000. However, the Examiner has not indicated consideration of the IDS filed July 2, 2003. For the Examiner's convenience, Applicants are re-submitting the IDS, originally filed on July 2, 2003, as evidenced by the attached dated postcard. Applicants respectfully request the Examiner to acknowledge consideration of the attached references.

Customer Number
29315

Application Serial No.: 09/704,565
Attorney Docket No.: 23439-034-402
Reply and Amendment Under 37 C.F.R. §1.111

If the Examiner believes, for any reason, that personal communication will expedite prosecution of this application, the Examiner is invited to telephone the undersigned at the number provided.

Dated: 18 Dec '03

Respectfully submitted,



Customer Number
29315

Sean L. Ingram
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Attorney Docket No.: 23439-034-402

Inventors: John DiDOMENICO *et al.*

Serial No.: 09/704,565

Filing Date: November 3, 2000

Title: REMOTE EMISSIONS SENSING SYSTEM AND METHOD WITH A COMPOSITE BEAM OF IR AND UV RADIATION THAT IS NOT SPLIT FOR DETECTION

Documents Filed:

- 1. Supplemental Information Disclosure Statement
- 2. Form PTO-1449
- 3. Copy of Supplementary European Search Report
- 4. Four (4) references



Sender's Initials: SLI/slt

Date: July 2, 2003



COPY



29315

PATENT & TRADEMARK OFFICE

PATENT

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Patent Application of:) Docket No.: 23439-034-402
John DiDOMENICO *et al.*)
Serial No.: 09/704,565) Confirmation No.: 5556
Filed: November 3, 2000) Examiner: Otilia Gabor
) Group Art Unit: 2878

For: **REMOTE EMISSIONS SENSING SYSTEM AND METHOD WITH A COMPOSITE BEAM OF IR AND UV RADIATION THAT IS NOT SPLIT FOR DETECTION**

SUPPLEMENTAL INFORMATION DISCLOSURE STATEMENT

Commissioner for Patents
P. O. Box 1450
Alexandria, VA 22313-1450

Sir:

Pursuant to the duty of disclosure under 37 C.F.R. §§ 1.56, 1.97 and 1.98, Applicants hereby make of record in the above-identified application the documents listed on the attached Form PTO-1449.

Applicants have listed publication dates on the attached PTO-1449 based on information presently available to the undersigned. However, the listed publication dates should not be construed as an admission that the information was actually published on the date indicated.

Applicants reserve the right to establish the patentability of the claimed invention over any of the information provided herewith, and/or to prove that this information may not be prior art, and/or to prove that this information may not be enabling for the teachings purportedly offered.

This Supplemental Information Disclosure Statement is being filed before the mailing date of a first Office Action on the merits. No certification or fee is required. 37 C.F.R. 1.97(b).

These documents were cited in a search report by a foreign patent office in a counterpart foreign application. Submission of an English-language version of the search report that indicates the degree of relevance found by the foreign office is provided.

It is respectfully requested that the Examiner initial and return a copy of the enclosed PTO-1449.

Respectfully submitted,

MINTZ, LEVIN, COHN, FERRIS, GLOVSKY
and POPEO, P.C.


By _____
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Attorney for Applicants

Dated: July 2, 2003



**INFORMATION DISCLOSURE CITATION
IN AN APPLICATION**

Form PTO-1449

Docket Number	Application Number
23439-034-402	09/704,565
Applicant(s)	
John DiDOMENICO et al.	
Filing Date	Group Art Unit
November 3, 2000	2878

U.S. PATENT DOCUMENTS

FOREIGN PATENT DOCUMENTS

REF	DOCUMENT NO.	DATE	COUNTRY	CLASS	SUBCLASS	Translation	
						YES	NO

OTHER DOCUMENTS (Including Author, Title, Date, Pertinent Pages, Etc.)

D GUENTHER, Paul L., *et al.*, "A Hydrocarbon Detector for the Remote Sensing of Vehicle Exhaust Emissions", *Review of Scientific Instruments*, Volume 66, No. 4, April 1995, pages 3024-3029.

EXAMINER _____ DATE CONSIDERED _____

EXAMINER: Initial if citation considered, whether or not citation is in conformance with MPEP Section 609; Draw line through citation if not in conformance and not considered. Include copy of this form with next communication to Applicant.



DOCUMENTS CONSIDERED TO BE RELEVANT		Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.7)
Category	Citation of document with indication, where appropriate, of relevant passages		
Y	<p>GUENTHER P L ET AL: "A HYDROCARBON DETECTOR FOR THE REMOTE SENSING OF VEHICLE EXHAUST EMISSIONS" REVIEW OF SCIENTIFIC INSTRUMENTS, AMERICAN INSTITUTE OF PHYSICS, NEW YORK, US, vol. 66, no. 4, 1 April 1995 (1995-04-01), pages 3024-3029, XP000501100 ISSN: 0034-6748 * figure 1 *</p> <p>---</p>	1-7	G01N21/35 G01N21/33 G01J3/10
Y	<p>US 5 563 420 A (SULLIVAN M E ET AL) 8 October 1996 (1996-10-08) * column 2, line 34 - column 3, line 12; figure 1 *</p> <p>---</p>	1-7	
Y	<p>US 5 498 872 A (STEDMAN DONALD H ET AL) 12 March 1996 (1996-03-12) * the whole document *</p> <p>---</p>	1-7	
A	<p>US 5 591 975 A (JACK MICHAEL D ET AL) 7 January 1997 (1997-01-07) * column 3, line 15 - column 4, line 9; figure 1 *</p> <p>-----</p>	1-7	<p>TECHNICAL FIELDS SEARCHED (Int.Cl.7)</p> <p>G01N G01J</p>
The supplementary search report has been based on the last set of claims valid and available at the start of the search.			
2	<p>Place of search MUNICH</p> <p>EPO FORM 1503 03/82 (PAC04)</p>	<p>Date of completion of the search 26 March 2003</p>	Examiner Consalvo, D
CATEGORY OF CITED DOCUMENTS		<p>T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document</p>	
<p>X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document</p>			

**ANNEX TO THE EUROPEAN SEARCH REPORT
ON EUROPEAN PATENT APPLICATION NO.**

EP 99 95 1468

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report. The members are as contained in the European Patent Office EDP file on. The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

26-03-2003

Patent document cited in search report		Publication date	Patent family member(s)		Publication date
US 5563420	A	08-10-1996	NONE		
US 5498872	A	12-03-1996	US 5401967 A US 5319199 A US 5210702 A US 5489777 A AU 656356 B2 AU 9170391 A CA 2099259 A1 DE 69131048 D1 DE 69131048 T2 EP 0564566 A1 JP 3347725 B2 JP 6505095 T WO 9212411 A1		28-03-1995 07-06-1994 11-05-1993 06-02-1996 02-02-1995 17-08-1992 27-06-1992 29-04-1999 28-10-1999 13-10-1993 20-11-2002 09-06-1994 23-07-1992
US 5591975	A	07-01-1997	US 5418366 A CA 2131865 A1 AU 673786 B2 AU 1162095 A CA 2141004 A1 EP 0681179 A1 JP 8043288 A KR 206682 B1		23-05-1995 11-03-1995 21-11-1996 16-11-1995 06-11-1995 08-11-1995 16-02-1996 01-09-1999



XP 000501100

8127 Review of Scientific Instruments
66(1995) April, No. 4, Woodbury, NY, US

A hydrocarbon detector for the remote sensing of vehicle exhaust emissions

Paul L. Guenther, Donald H. Stedman, Gary A. Bishop, Stuart P. Beaton,
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(Received 4 January 1994; accepted for publication 19 December 1994)

*P-324-3029
-6*

A new remote sensor for measuring on-road carbon monoxide, carbon dioxide, and hydrocarbon exhaust emissions in under 1 s from vehicles passing the sensor is described. The new design adds the capability for measuring exhaust hydrocarbons and eliminates the need for liquid-nitrogen-cooled detectors while improving upon the overall signal to noise. Under typical field operating conditions, sensitivity to 0.05% propane with a precision of 0.014% propane is observed. Two types of water interferences important to the measurement of exhaust hydrocarbons are reported. The water vapor present in all auto exhaust causes a small positive bias dependent on the analytical wavelength chosen. A much larger interference is caused by liquid water (often called "steam") plumes seen behind cold vehicles at low temperatures. © 1995 American Institute of Physics.

I. INTRODUCTION

While many cities such as Denver suffer from failure to attain air quality standards due to carbon monoxide (CO) pollution, many others fail to meet standards due to ozone pollution. Hydrocarbon (HC) emissions from motor vehicles are of concern since some are themselves toxic and, together with oxides of nitrogen, they play a role in the creation of urban ozone. Close to their emissions source, exhaust emissions of nitric oxide (NO) from vehicles remove ozone and thus generate nitrogen dioxide (NO₂). Through a complicated series of reactions involving odd hydrogen free radicals and sunlight, the presence of HCs results in a net downwind formation of ozone and other components of photochemical smog. These HCs also provide nighttime reservoirs of NO_x and free radicals which are quickly released upon photolysis the next morning.¹

With initial support from the Colorado Office of Energy Conservation, the University of Denver developed an infrared (IR) remote monitoring system for automobile CO exhaust emissions which has been described in detail elsewhere.² The University of Denver CO remote sensor has been given the acronym "FEAT" for fuel efficiency automobile test because significantly improved fuel economy results when rich-burning (high CO and generally elevated HC) vehicles are tuned to a more stoichiometric air/fuel ratio. Results from many locations have consistently shown that half of the on-road light duty CO emissions are contributed by less than 10% of the vehicles.³⁻⁷ These vehicles are referred to as gross polluters. Data collected from vehicles tested using a dynamometer show similar distributions for HCs.^{8,9} The detection and successful repair of these on-road gross polluters provides an opportunity to devise new and cost-effective motor vehicle emission reductions strategies.¹⁰ On-road emissions are, after all, the parameter which on-road motor vehicle programs are attempting to control.

Several limitations of the initial instrument design² included the use of liquid-nitrogen-cooled indium antimonide detectors, a rotating gas filter correlation cell which pre-

cluded the simultaneous measurement of CO and reference signals, and 2 ft focal length lens optics which greatly increased the size of the detector unit. The desire for improvement in these areas along with an interest in adding the capability to measure HC exhaust emissions led to the design of the new instrument described herein.

II. EXPERIMENTAL SECTION

A. Instrument design

Major design changes have been made with the detectors, optics, and associated electronics. The new instrument uses four Peltier cooled lead selenide (PbSe) detectors, one each for reference, CO, CO₂, and HC. The use of electrical cooling eliminates the need for the liquid nitrogen. The optical system takes advantage of reflective as opposed to refractive optics and uses a motorized 12-sided polygon mirror in place of the beam splitter. Rather than receiving part of the signal all of the time, the elimination of beam splitters enables the detectors to receive all of the signal part of the time.

Figure 1 shows a schematic diagram of the optical bench. The incoming IR light is collected by a spherical 2 in. diameter f/6 mirror (Edmund Scientific). The IR beam is focused onto the surface of a 12-sided polygon mirror spinning at 12 000 rpm (Lincoln Laser P/N 1-3-2008-100 with driver card DC-5 1-3-1486-100H) which maintains an effective chopping frequency of 2400 Hz. The expanding beam from the spinning mirror is collected sequentially by a series of four spherical mirrors (2 in. diameter f/0.64) which focus the scanning beam onto the four Peltier cooled PbSe photoresistive detectors (Cal-Sensors model BT1S-18T). Each detector has an interference filter mounted directly over it to select the desired wavelength of light (filters from Barr Associates; see Table I). The detector and filter temperatures are maintained through feedback control at approximately -15 °C. This temperature represents the coolest temperature for which we were able to control the detector environment under ambient temperatures up to 38 °C.

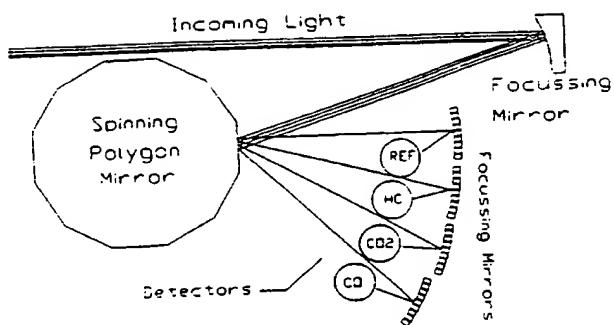


FIG. 1. Diagram of the optical components of FEAT 3 series containing the HC channel. Detectors are Peltier cooled PbSe with built-in interference filters. See Table I for filter bandpasses for each channel.

Each detector produces a 2400 Hz pulse train. Using an optical reference coupled to the spinning polygon, integration gates are set to accept equal time periods of signal (peak) and base line. The outputs of the two integrators are sent to a difference amplifier and the result is stored on a sample and hold capacitor which is reset every 5 ms. The dc output of the sample and hold circuit is filtered at 100 Hz, digitized (Scientific Solutions Labmaster 12-bit ADC), and analyzed by a personal computer.

The process by which the detector signals are converted to %CO and %CO₂ has been fully described elsewhere.¹¹ The HC data are converted and processed in an analogous manner to the earlier instrument.

B. Calibration

Calibration requires development of a curve defining the absorption observed from known optical depths of the gas of interest. The procedure consists of using mass flow controllers, coupled to an 8 cm path-length IR cell, to regulate the concentrations of CO, CO₂, or propane diluted with N₂. Absorption measurements were made at ten different concentrations to define the calibration curve. The equations for the observed curves are linear for propane and second-order polynomials for CO and CO₂. The calibration curves are similar for all instruments since they are primarily a function of the interference filter parameters and spectroscopy.

Typical nonlinear calibration curves (CO and CO₂) for the first unit are shown in Fig. 2. The propane calibration is accurately represented by the linear expression %Propane = 10.1 ($I_0/I - 1$). I_0 is the reference normalized voltage with no propane in the flow cell and I is the reference normalized voltage with a known concentration of propane present. The

TABLE I. Bandpass characteristics of the interference filters chosen for use in the FEAT 3 series of instruments. Bandwidth is full width at half height.

Gas detected	Bandpass center (-30 °C)	Bandwidth
CO ₂	2331 cm ⁻¹	120 cm ⁻¹
CO	2165 cm ⁻¹	90 cm ⁻¹
HC	3030 cm ⁻¹	140 cm ⁻¹
Reference	2577 cm ⁻¹	90 cm ⁻¹

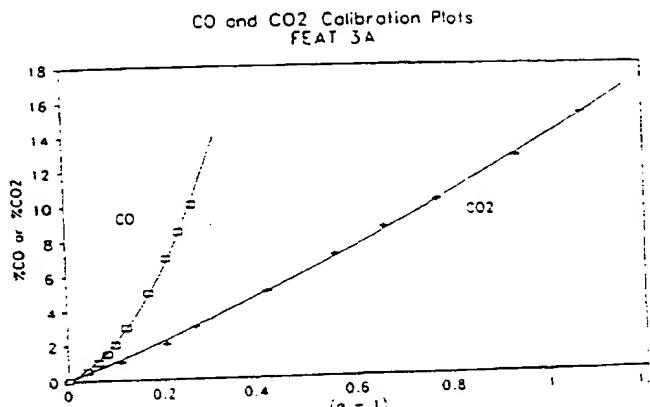


FIG. 2. CO and CO₂ calibration plots for the first FEAT 3 unit produced. "a" represents normalized reference signal divided by either normalized CO or CO₂ signal.

first nonpropane calibration data to be collected were for hexane. This is analogous to the procedure carried out by the manufacturers of conventional tail-pipe analyzers who carry out a one-point calibration comparison between propane and hexane for use in converting the analytical results from propane to hexane. The comparison for the filter centered at 3030 cm⁻¹ resulted in a difference in the slopes of 1.74 ± 0.2, indicating that our results in concentration of propane need to be divided by that factor to become the equivalent concentration in hexane. Since the instrument is calibrated with propane, we believe all results should be reported as percent propane equivalents even though this is counter to the industry standard practice of calibrating with propane and reporting in hexane units.

C. Spectroscopy of hydrocarbons

The bandpass chosen for the reference detector of the new instrument was centered at 2577 cm⁻¹ because it was anticipated that no components in the atmosphere or engine exhaust absorb in this wavelength region. This wavelength is also used by conventional emissions analyzers.¹² Since FEAT was intended to reproduce these instruments' measurements, a filter with a bandpass centered at 3030 cm⁻¹ was chosen for the HC channel as this was thought to be the bandpass used by existing emissions analyzers. Absorbance in this region is primarily due to stretching of carbon hydrogen bonds.

Dry air has no absorbance in this region. There are some absorption lines from water vapor and the amount of overlap of the 3030 cm⁻¹ filter with different hydrocarbons varies. There is no single best wavelength with which to determine all HCs of interest. Figure 3 shows the overlap of the chosen filter with propane. Overlap with methane is quite good; however, the absorption lines are narrow and thus instrument sensitivity to methane is low. Propane is the gas used to calibrate both our instrument as well as conventional tail-pipe probes. The filter is centered at too high an energy to have maximum propane sensitivity. The overlap with various aromatics such as toluene is very good but they are less absorbing per molecule than the alkanes.

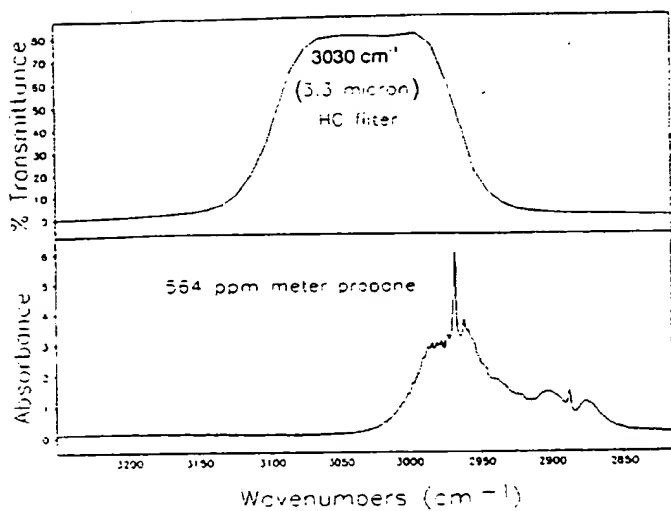


FIG. 3. Spectrum of 564-ppm meter propane in 1 atm of nitrogen shown below a schematic diagram of the cold 3030 cm^{-1} HC filter bandpass.

Ideally one would like to account for the total smog forming reactivity of the hydrocarbons emitted by each vehicle. However, due to the diversity of molecules present in fuel and the exhaust, and their varied absorption spectra, it is not possible for any single wavelength to accurately represent all molecules (or even the total carbon content) in the vehicle exhaust. Flame ionization detectors are used for motor vehicle certification tests; however, they are approximately carbon counters, and do not reflect reactivity or toxicity. Thus even if a wavelength could be found which provides measurements that exactly match a flame ionization detector, the data would not correctly predict ozone formation or estimate so-called "air toxics" since the reactivities and toxicities of the various exhaust molecules per carbon atom vary over several orders of magnitude.¹³

III. RESULTS

Table II shows the slopes of the linear propane calibrations for five of the new instruments. A smaller slope indicates a greater sensitivity to propane. The first four calibrations show a similar slope plus or minus about 20%. After the fifth unit of the new series (designated as 3E in Table II)

TABLE II. Comparison of linear calibration slopes for the first five instruments. A lower number indicates a higher sensitivity to propane. Instrument 3E was much less sensitive than its predecessors prior to changing the HC filter bandpass.

FEAT unit	Calibration slope	HC filter bandpass
3A	10.1	3030 cm^{-1}
3B	6.8	3030 cm^{-1}
3C	9.1	3030 cm^{-1}
3D	6.2	3030 cm^{-1}
3E	18.4	3030 cm^{-1}
3A	3.9	2941 cm^{-1}
3B	3.8	2941 cm^{-1}
3E	3.9	2941 cm^{-1}

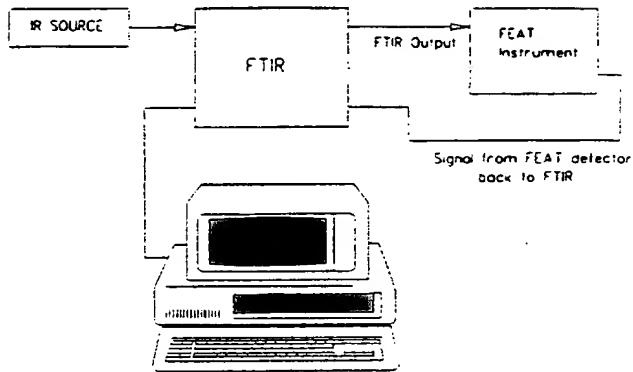


FIG. 4. Schematic diagram of setup of experiment designed to measure the in-use bandpass of the FEAT interference filters. Signal output from the FEAT detector was sent back to FTIR bench, bypassing the FTIR's own detector.

was calibrated and found to be almost half as sensitive to propane as our previously least sensitive instrument, a further investigation was initiated.

The detectors are constructed with the Peltier cooler attached to the back of the PbSe detector with the interference filter attached to the front side of the detector. The detector and presumably the filter are operating at a temperature of around $-15\text{ }^{\circ}\text{C}$. Up to this point we had only the filter manufacturer's specification sheet by which to judge the filter characteristics. The manufacturer cut a single filter into many small disks with one of the small disks being installed on each detector. We assumed that each piece of the disk uniformly shared the bandpass characteristics of the parent filter. Also, the bandpass of the filter is affected by temperature and, in view of the cooling geometry, we did not know at what temperature the filter was being maintained. In order to investigate this phenomenon a system was designed by means of which the bandpass could be determined under actual operating conditions. A modulated IR beam was passed through the interference filter and on to each detector while the instrument was running (with the spinning polygon disconnected). A Bomem MB100 FTIR was used to produce the modulated IR radiation and the signal from the detectors was routed back into the Bomem in place of its own detector signal. With this arrangement we were able to see for the first time the exact bandpass of the filter/detector combination under actual operating conditions. Figure 4 shows a diagram of the setup.

The bandpasses of three of the HC detectors (units 3B, 3D, and 3E) were compared. The results are shown in Fig. 5. 3E stands out as being quite different from the other two, being shifted to longer wavenumbers, even though its filter was cut from the same blank and was sold with the same specifications. Looking again at Fig. 3 (showing the overlap of the 3030 cm^{-1} filter with propane), it can be seen that small shifts in the filter bandpass could cause large changes in the amount of overlap with the propane absorption spectrum. The direction of this shift is compatible with the observed lack of sensitivity of unit 3E.

Initial calibration data showed that a 1% reduction in the HC signal relative to the reference signal will be interpreted

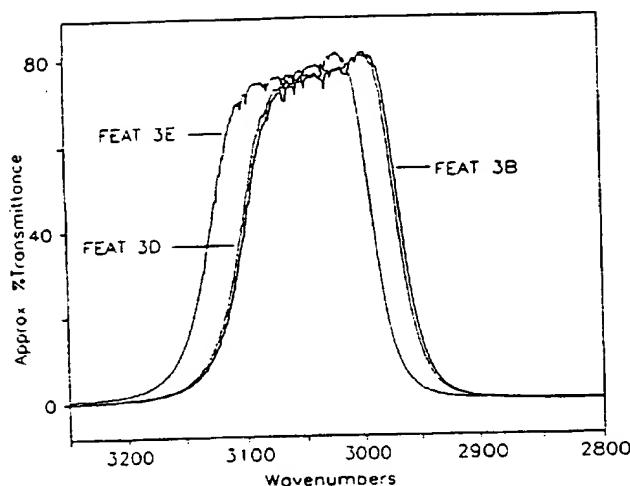


FIG. 5. FEAT 3 HC detectors' view of the world. Absorption dips seen at top of the transmission curve are due to atmospheric water vapor over a 3 ft path. These peaks are not fully resolved at 1 cm^{-1} instrument resolution.

as 0.1% HC (propane). If we wish to achieve a detection limit of 0.01% HC (propane), then a 0.1% reduction in HC voltage relative to the reference must be detectable, and the relative signal stability and noise combined must be less than one part in 1000 for the HC channel relative to the reference and CO_2 channels. In any given plume the ratios of the constituents remain constant even though the absolute concentration of the components varies. Remote sensing works by measuring the pollutant plume relative to that of CO_2 . The smaller the cross section of plume observed by the instrument, the less CO_2 is measured and thus correspondingly less CO and HC will be measured. It is not unusual for the measured plume of exhaust behind a vehicle to contain only one hundredth of the optical depth of CO_2 which would be observed if pure exhaust were confined in an 8 cm cell. This typical dilute plume in our 8 cm calibration cell would be measured at 0.15% CO_2 rather than at 15% had the entire plume been captured. Thus an ideal noise level in the diluted plume for 0.01% HC detection needs to be $100\times$ better (i.e., one part in 10^5) because the entire plume has not been captured.

For the CO channel, the observed noise levels are quite tolerable as they translate into %CO readings well into the low emitting vehicle range. For the same weak CO_2 plume mentioned above with an 8 cm gas cell concentration of 0.15%, the S/N need only be five parts in 10 000 to adequately measure a 0.5% CO plume (almost $10\times$ under the emissions of the CO gross polluters, vehicles which are responsible for about half the total CO emissions).

In typical use when no exhaust is present, the standard deviation of 50 10-ms data points is 10^{-3} V with an average signal of 7 V. With the averaging process in the data analysis, this brings the noise down close to one part in 10^5 .

A. Water interference

The possibility of interference from water vapor in the exhaust was examined more closely because water does have some absorption lines in the bandpass being used for HCs.

Calculation using a spectrum library file for air at 2% absolute humidity, using the 3030 cm^{-1} bandpass of the filter/detector combination (seen in Fig. 3), showed a 7% anticipated signal reduction arising from setting the instrument across 10 m of roadway. A further 0.4% signal reduction relative to the HC voltage would be caused by a vehicle emitting about 15% water vapor through a 5 cm diameter tail pipe. A calculation using dry air with only typical exhaust humidity added led to a similar calculated signal reduction of 0.6%. The library spectra show partial absorption, but the resolution is only 1 cm^{-1} . Thus, we originally thought that a higher resolution analysis would show the water lines to be fully absorbed at this concentration and any additional water vapor from vehicle exhaust at typical humidities would contribute negligibly. If, however, the modeled calculations are correct, then a water vapor interference using a filter centered at 3030 cm^{-1} would be anticipated. The added absorption would be interpreted as an interference of about 300 ppm propane (0.03%) independent of ambient water absorption.

B. Validation of instrument

In May of 1991, three instruments (units 3B, 3D, and 3E) were tested versus an instrumented General Motors (GM) vehicle operating in cruise control with on-board tailpipe emissions measuring ability (fully described by Ashbaugh *et al.*¹⁴). The on-board measuring device also used NDIR but most of the water in the exhaust is removed before sampling. All three instruments show excellent agreement with GM for CO, with slopes for the comparisons ranging from 0.97 to 1.2 with r^2 values for all instruments >0.99 . Regressions for the HC channel for units 3B and 3D (unit 3E suffered damage to its focusing mirror in transit and the HC data were unavailable) are 1.3 and 1.6, respectively, and the reported r^2 values were 0.85 and 0.82, respectively.¹⁴ Both instruments showed an intercept on the FEAT HC axis when compared to the GM vehicle of $0.029\%\pm0.04\%$ and $0.046\%\pm0.06\%$ propane for 3B and 3D, respectively.

IV. DISCUSSION

To improve the original instrument and eliminate some of the interferences, changes to the instruments in the form of electronic and optical improvements were performed. The HC filter was switched to one with a bandpass centered at 2941 cm^{-1} , in order to reduce the effects of water vapor interference. This filter's bandpass and a comparison with spectra of water vapor and propane can be seen in Fig. 6. The shift to smaller wavenumbers results in an improved response to propane and analogous paraffins. Slopes from calibration measurements indicate it to be about $2.5\times$ more sensitive than the 3030 cm^{-1} unit, as shown in Table II.

Modern catalyst equipped vehicles when warmed up and operated under load have been shown in dynamometer studies to emit very low levels of CO and HC. When looking at fleet data for those vehicles with the lowest CO emissions, it is likely that those vehicles are mostly emitting low levels of HCs as well. The distribution of HC emissions in data collected on March 11, 1991 in Denver, Colorado for vehicles with less than 1% CO show a peak around 0.03% propane

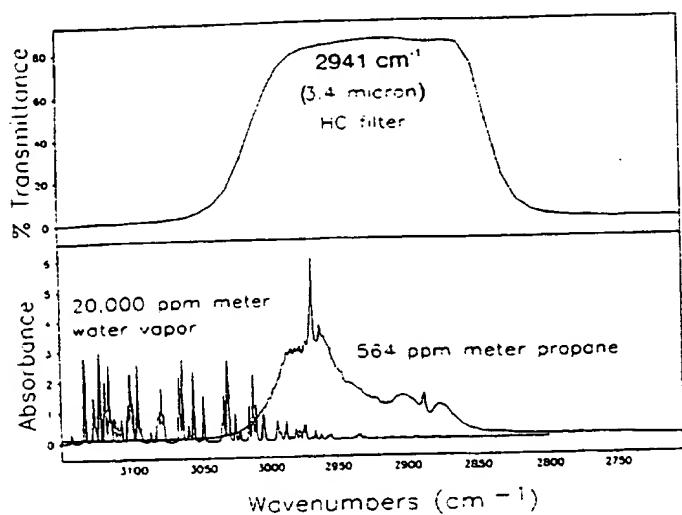


FIG. 6. Comparison of 2941 cm^{-1} HC filter bandpass to spectra of 2% absolute humidity H_2O (1 m path) and 564 ppm meter propane which show good overlap with propane and reduced overlap with water vapor.

which represents the most frequent apparent HC emission. A possible explanation for this result is an interference caused by water vapor in the exhaust. The same instrument was used to collect another set of data containing around 2000 vehicles in El Monte, California on June 8, 1991. These data show that the HC emissions, for the part of the data set containing vehicles with emissions of less than 1% CO, averaged 0.032% HC. This intercept is in agreement with the Denver data.

On May 3, 1991 an experiment was run in El Monte, California in which the same 3030 cm^{-1} HC system was used to measure emissions from a vehicle on a dynamometer. Under these circumstances the introduction of exhaust gas into the optical system is different. The exhaust plume is pumped through a long tube at ambient temperature into a water drop-out chamber prior to being released via a solenoid valve into the IR light path. This process allows most of the moisture in the exhaust to be removed prior to the measurement. The vehicle on the dynamometer was operated in a wide range of driving modes, steady-state and transient, with and without induced malfunction, including intentional rich and lean operation. The average HC emissions of several hundred measurements while the vehicle was emitting less than 0.15% CO, and thus would be expected to have low HC emissions, was 0.0057% (57 ppm). The lack of moisture content in the exhaust is believed to be the reason for the low average %HC measured.

We had the opportunity to perform an experiment in the parking lot near our lab in which we drove a low mileage 1 yr old vehicle by a FEAT unit under steady-state conditions. This FEAT unit (3E) had a new 2941 cm^{-1} filter and the average HC measurement for 30 passes by the vehicle was 0.0065% (65 ppm). Improvements in precision were observed in this parking lot experiment. The same vehicle was driven under similar conditions by FEAT 3B while it still had the original 3030 cm^{-1} filter. The standard deviation of the %HC measurements for this vehicle was about double that of

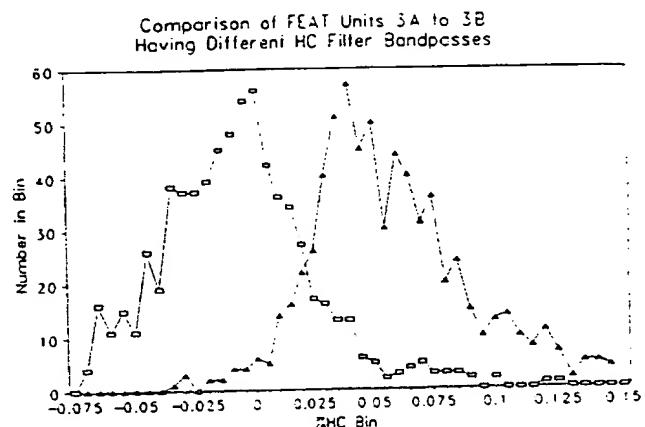


FIG. 7. Data showing distribution of %HC readings for vehicles with under 1% CO measured simultaneously with two FEAT units. Effect of HC filter change can be seen in the position of the center of the FEAT 3A histogram (squares, 2941 cm^{-1} filter) compared to the FEAT 3B histogram (triangles, 3030 cm^{-1} filter).

FEAT 3E's standard deviation, while both instruments measured nearly identical %CO values. Recent drive-by studies with GM's instrumented vehicle performed at the Fort McHenry Tunnel in Baltimore, Maryland show more evidence of instrument improvement with the change in filter bandpass.¹⁵ In this comparison FEAT 3A, with the 2941 cm^{-1} filter, was measured to have a standard error of the fit of 0.02% propane which includes any imprecision from the GM on-board vehicle monitoring system. When observing vehicles driving on uphill on-ramps, the detection limit for the revised FEAT with a 2941 cm^{-1} HC filter is 0.05% with a noise of $\pm 0.014\%$ propane over a typical field-use path length of 10–15 m.

An instrument with a 2941 cm^{-1} bandpass filter (FEAT 3A) was used to measure a fleet of on-road vehicles. Because on-road remote sensing measurements are dependent on the slope of a line (i.e., the HC to CO_2 ratio) and because the data contain noise, it is quite possible that for a zero emission vehicle this slope could be slightly negative. When looking at that part of the fleet with CO emissions <1%, the average HC emission was $-0.0081\%\text{HC}$ (−81 ppm). Simultaneously, a second FEAT instrument (FEAT 3B) was operating and collecting data in such a manner that the two instruments were measuring the same vehicle at virtually the same instant. FEAT 3B still had the 3030 cm^{-1} filter and the most frequent HC emissions measured were between 0.04% and 0.05% HC (400–500 ppm). The results can be seen graphically in Fig. 7. The %HC data from the two instruments were divided into bins of 0.005% HC (50 ppm propane) and the number of vehicles in the bin is shown on the Y axis. The total number of paired HC exhaust emissions with <1% CO in this experiment was 696. Since these two instruments were measuring the same exhaust plume at the same time, we take that as proof that the large change in intercept was not caused by the small change in calibration sensitivity and was therefore presumed to be caused by water vapor interference.

A further advantage of shifting the filter bandpass was observed when it was discovered that a second source of water interference exists. When the ambient relative humidity is high and temperature is below 5 °C, stop and go driving allows the exhaust system of many vehicles to cool off enough so that a plume of water droplets (often called "steam") emerges from the tail pipe. This "steam" plume is measured by FEAT as an elevated HC emission and occurs due to the IR absorption by liquid water which is red shifted and broadened relative to gas phase water so as to inevitably overlap the carbon-hydrogen stretching wavelength region.

The report by Stedman *et al.*⁶ describes the observation which led to this understanding. Unexpectedly high (1% propane and higher) HC emissions were found in late model (1988-90 measured in 1991) Honda Civics with 1.5 L engines. Experiments performed in Denver on a similar vehicle revealed that, when driven around our parking lot at 352 °C at 12-20 mph, after about 100 s (four passes) the CO readings became very low (<0.3%) but the HC readings remained very high and erratic for as long as we left the conditions unchanged. A small steam plume was visible on each occasion. The vehicle was then taken out to the freeway for several minutes of high-speed driving. Upon return, CO and HC readings were observed in the normal range for new vehicles (%CO<0.3 and %HC<0.08).

Further examination of the videotapes of the Chicago measurements confirmed the coincidence of late model, high HC reading, 1500 cc Honda Civics with observable steam plumes. The fact that this interference was caused by visible steam was fully confirmed by a laboratory experiment in which breath exhaled over a liquid-nitrogen container read 1% propane equivalents or more, while uncooled breath always read <0.05%. Moving the HC filter bandpass to 2941 cm⁻¹ does help to diminish this problem; however, future instruments are being designed to avoid the problem by detecting the presence of steam plumes.

The current generation of FEAT instruments is able to correctly identify the gross polluters with HC emissions greater than 0.1% or 0.2%, measured as propane.^{10,16,17} Elimination of the water vapor interference improved the ability of fleet remote sensing readings to contribute to observing changes in and distributions of mobile source inventories. The fact that small differences in fleet average HC emissions can now be distinguished is shown by the results presented in Zhang *et al.*¹⁸ Further details of this work can be found in the University of Denver M.Sc. thesis of P. L. Guenther.¹⁹

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